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PHOTOCATALYTIC OXIDATION OF METHYL ORANGE DYE OVER TITANIA NANOCATALYST

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Abstract. In this study, the ability of titania dioxide nanoparticles (TiO_2) to remove methyl orange dye in aqueous solution was investigated. The effects of TiO_2 dosage (i.e. 0.4, 0.8, 1.2, 1.6 and 2 g), pH (i.e. 4, 6, 7, 8, 10 and 12) temperature (30, 40 and 50°C) and light source (i.e. UV, sunlight and dark room) on the removal of methyl orange dye were studied. The experiments were conducted under the UV light irradiation with the presence of air bubbling. The samples were analyzed using UV-vis spectrophotometer at wavelength of 467 nm. From this study, it was found that the TiO_2 dose, pH, temperature and the presence of light had a strong effect on the removal of dye. The removal of dye was optimum at TiO_2 loading of 2.0 g, pH of 4, temperature of 30°C and under UV light condition.

Keywords: Methyl orange dye; titania dioxide; photocatalytic oxidation; pH; temperature

Abstrak. Dalam kajian ini, kebolehupayaan titanium dioksida (TiO_2) untuk menyingkirkan pewarna metil oren daripada larutan telah dikaji. Kesan-kesan dos TiO_2 (iaitu 0.4, 0.8, 1.2, 1.6 and 2 g), pH (iaitu 4,6,8,10 dan 12) suhu (iaitu 30, 40 and 50°C) dan sumber cahaya (UV, cahaya matahari dan bilik yang gelap) terhadap penyingkiran pewarna metil oren telah dikaji. Eksperimen telah dijalankan di bawah radiasi UV dengan kehadiran oksigen terlarut. Sampel telah dianalisa menggunakan UV-vis spektrofotometer dengan panjang gelombang 467 nm. Daripada kajian ini, telah didapati bahawa dos TiO_2, pH, suhu dan kehadiran cahaya memberikan kesan yang ketara terhadap penyingkiran pewarna. Penyingkiran pewarna adalah paling optimum pada dos TiO_2, 2 g, pH, 4, suhu, 30°C dan dibawah cahaya UV.
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Kata kunci: Pewarna metil oren; titanium dioksida; pengoksidaan fotomangkin; pH; suhu

1.0 INTRODUCTION

Dyes containing azo-aromatic groups are highly dispersible pollutants. They contribute to water toxicity and represent an increasing danger for the

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environment and human beings. These effluents discharged from various industries (e.g. textile, paper, leather, food, etc.) are known to be toxic [1], carcinogenic [2],mutagenic [3], teratogenic [4], and their release in the environment is a considerable source of non aesthetic pollution since the existence of low concentrations of dyes is clearly visible. Thus, the removal of these colored compounds from wastewater is an important target from the environmental point of view. However, this process faces a major problem represented in the high stability of these azo dyes in aqueous media and their resistance to light and oxidation agents [5]. Conventional treatment methods for the removal of dyes in wastewater include physical, chemical and biological processes such as adsorption [6], coagulation [7], oxidation [8], reduction [9], filtration [10], and biological treatment [11]. The physical adsorption process at solid-liquid interface is known to be a powerful method for decreasing the concentration of soluble dyes in effluents and has the advantage of being efficient and economic.

Photocatalytic oxidation (PCO) is viewed as an attractive option to be the alternative. PCO is an oxidation process that could stimulate chemical reaction with the help from certain catalysts in the presence of UV radiation. Semiconductors such as TiO_2, Fe_2O_3, ZnO, ZnS, CdS and WO_3 have been known to possess photocatalytic character. Among them, titania dioxide (TiO_2) is the most widely used as an inorganic catalyst for photocatalytic oxidation process. It is because TiO_2 has high in stability, poses non-toxic character and very effective. The photocatalyst, TiO_2, has a wide bandgap (3.2 eV) semiconductor which is corresponding to radiation in the near UV range. Upon the absorption of this UV energy, TiO_2 particles will form a paired electron (e^-) and hole (h^+) in the conduction band and valence band, respectively. The positive hole is able to oxidize a water molecule to hydroxyl radical (OH^{-1}) which is is a powerful oxidant. The oxidation of organic contaminants seems to be mediated by a series of reactions initiated by hydroxyl radical on the TiO_2 surface. For the photo-oxidation reaction to occur, both TiO_2 and a UV light source are necessary [12].
Therefore, in this study, the effectiveness of TiO_2 on the photocatalytic oxidation of methyl orange dye was studied. The effects of TiO_2 dosage, temperature, pH and source of the light on the removal of methyl orange dye were investigated.

2.0 EXPERIMENT

2.1 Materials

Titania oxide (TiO_2) was purchased from Sigma-Aldrich and had a composition close to 80 % anatase and 20 % rutile. The BET surface area of TiO_2 determined by nitrogen adsorption at 77 K was 45 $m^2.g^{-1}$. Methyl orange dye, acetic acid and potassium hydroxide (0.2 M) were also purchased from Sigma-Aldrich Co.

2.2 Methyl Orange Dye Preparation

Methyl orange dye solution was prepared by mixing 10 mg of dye in 1000 mL of distilled water. Then the solution was diluted until it reached to 10 ppm. The concentration of dye solution was kept constant at 10 ppm throughout the experiment.

2.3 Photocatalytic Reaction

The photocatalytic reaction was performed in glass vials placed in a controlled-temperature shaking water bath operating at 200 rpm. The sample was exposed to UV irradiation light from a medium pressure 250 W Hg lamp (λ_{max} = 365 nm). The sample was also been supplied with continuous O_2 flow with a flow rate of 200 ml/min. The reaction was conducted for 80 minutes at different temperature, 30, 40 and 50°C. The aliquots were carefully withdrawn from the solution and the solution absorbance was measured using JENWAY 6305 UV-vis spectrophotometer at wavelength of 467 nm.

The effect of pH was studied after the adjustment of the dye solutions pH between 4 and 12 using dilute HCI and NaOH solutions. The dosage of TiO_2 was studied in the range of 0.4 to 2 g.

The effect of conditions on the reaction was studied by performing the reaction under sun light and in a dark room. Under the sun light condition, the samples were exposed to sun for 80 minutes at noon. Reaction under a dark room was achieved by placing the sample inside the close cupboard for 80 minutes as well.

2.4 Determination of Concentration and Percentage of Dye

The percentage removal of dye was calculated by using equation (1).

$$\% \text{ dye removal} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 and C_t is concentration at time zero and t, respectively.

The concentration of dye (i.e. initial and at time t) can be calculated using equation (2) which is obtained from a calibration method.

$$y = 0.064x - 0.019 \quad (2)$$

where, x and y represents concentration of dye and absorbance, respectively.

3.0 RESULTS AND DISCUSSIONS

3.1 Effects of Titanium Dioxide Loading

Figure 1 shows the effect of TiO_2 dosage on percentage removal of methyl orange dye. As can be seen, the dye removal increased with the increasing of TiO_2 dosage with the highest removal was about 38% (i.e. achieved using 2 g of TiO_2). This shows the availability of the adsorption sites when large adsorbent quantities were used. Thus, enhances the photocatalytic degradation process [13, 14].

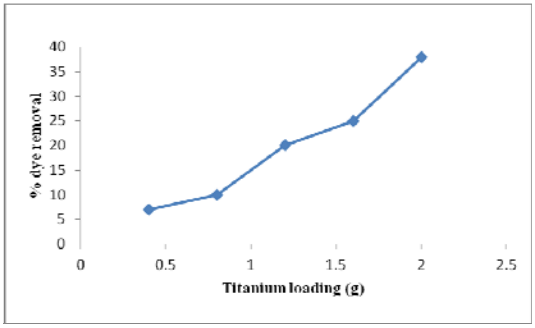

Figure 1 Effect of titanium dosage on the percentage removal of dye. Operating condition: pH was at pH 4 and temperature was 30°C

3.2 Effects of pH

Figure 2 shows the effect of pH on percentage removal of dye. The pH of the solution has a significant effect on the surface properties of TiO_2 catalyst, which include the surface properties of the particles, the size of the aggregate of catalyst particles it forms, and the band edge position of TiO_2 [15]. The photocatalytic reaction in general is pH dependent because the reaction takes place on the surface of the catalyst, although the rate varies by less than first order of magnitude between 2 and 12 [15]. From the results obtained, it has clearly shown that the dye removal was more effective at acidic solution than that at alkaline solution.

The interpretation of the pH effect on the photocatalytic process is very difficult because of its multiple roles such as electrostatic interactions between the semiconductors surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionization state of the state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions respectively, as shown in equations (3) and (4), respectively.

$$TiOH + H^+ \rightarrow TiOH_2^+ \tag{3}$$

$$TiOH + OH^{-1} \rightarrow TiO^{-1} + H_2O \tag{4}$$

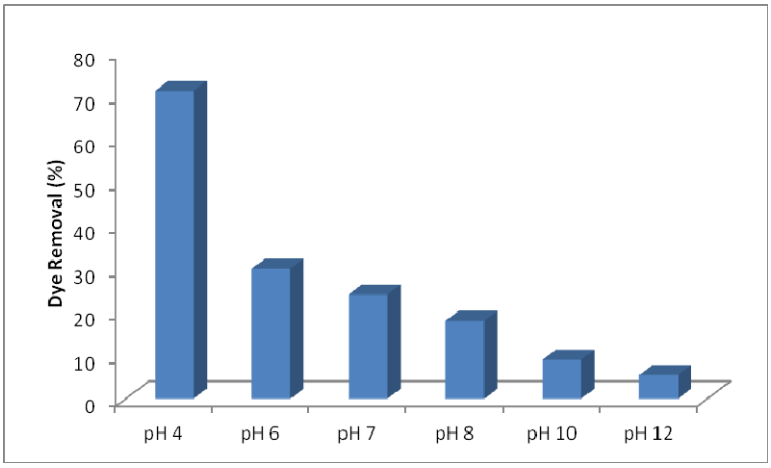

Figure 2 Effect of pH on the percentage removal of dye. Operating condition: Temperature was at 30°C and TiO_2 dosage was 0.4 g

The degradation of dye compound was better at lower pH (i.e. the removal of dye achieved in this study was the highest at pH 4, which is about 70 %) and it is believed due to the surface charged of TiO_2. The point of zero charge of TiO_2 oxide is 6.0 [16], thus, TiO_2 exhibits a positive zeta potential at pH values lower than 6.0 (i.e. TiO_2 surface becomes negatively charged at pH greater than 6.0 and the negatively charged surface groups increases as pH increases). Accordingly, an electrostatic repulsion between the negatively charged dye and the surface groups took place and led to a significant decrease of the adsorption capacity of TiO_2 catalyst. This explains the reason why the percentage of removal (i.e. adsorption capacity) was low at alkaline condition (i.e. high pH).

3.3 Effects of Temperature

The photocatalytic oxidation process was studied at various temperatures of 30, 40 and 50°C (refer to Figure 3). The solution temperature can affect to both photocatalyst and bulk properties including the dye molecules [17]. Overall, the percentage removal of the dye decreased as the temperature increased. At 30°C, the removal of dye was the highest which is about 68 %. However, the removal of dye was the lowest at temperature of 50°C, which is less than 5 %. This shows that the adsorption process is exothermic and this fact explains the diminution of adsorption capacity (i.e. low removal) with the augment of temperature [17].

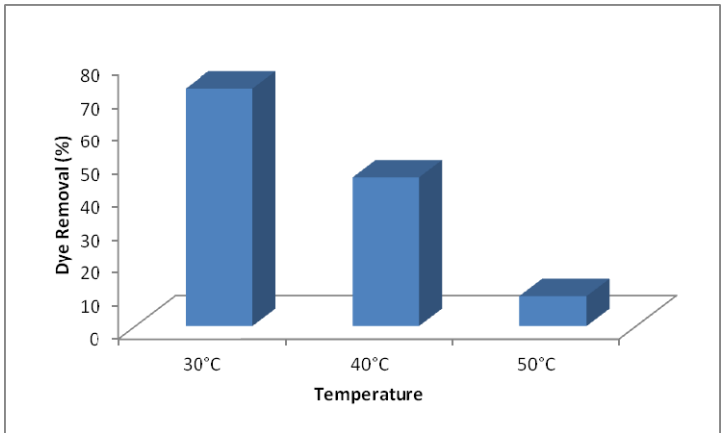

Figure 3 Effect of temperature on the percentage removal of dye. Operating condition: pH was at pH 4 and TiO_2 dosage was 0.4 g

3.4 Effects of Conditions

The photocatalytic oxidation process was studied at various conditions; dark room, under UV light and under the sunlight (refer to Figure 4). As can be seen, the percentage removal of dye was the best under the presence of UV light (60 %), followed with the sunlight (33 %) and without light (8 %).

UV light gave better results since the light actively excite the TiO_2 to remove the dye. Furthermore, UV light was able to give constant irradiation so that the catalyst can actively remove the dye with high effectiveness rather than the sunlight or darkroom. The dark room showed a poor result because there was no light that available to excite the TiO_2 catalyst. The results revealed that both TiO_2 and light source are equally important in the photocatalytic reaction [12].

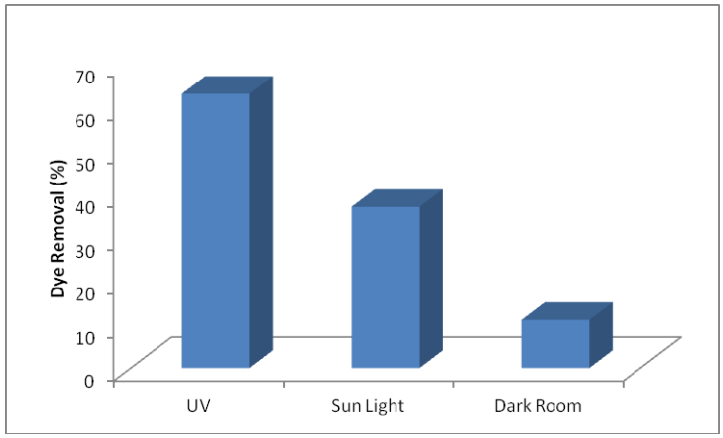

Figure 4 Effect of condition on the percentage removal of dye. Operating condition: pH was at pH 4 and TiO_2 dosage was 0.4 g

4.0 CONCLUSION

A detailed feasibility study has been carried out on photocatalytic oxidation of methyl orange dye using TiO_2 catalyst under UV light radiation. It was found that the TiO_2 dose, pH, temperature and the presence of light had a strong effect on the removal of dye. From this study, the removal of dye was optimum at TiO_2 loading of 2.0 g, pH of 4, temperature of 30°C and under UV light condition.

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